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Advanced Membranes for Vanadium Redox Flow Batteries (VRB) September 17th, 2014

Cy Fujimoto

Tom Zawodzinski, Zhijiang Tang, Alan Pezeshiki,
Travis Anderson and Harry Pratt



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Acknowledgements

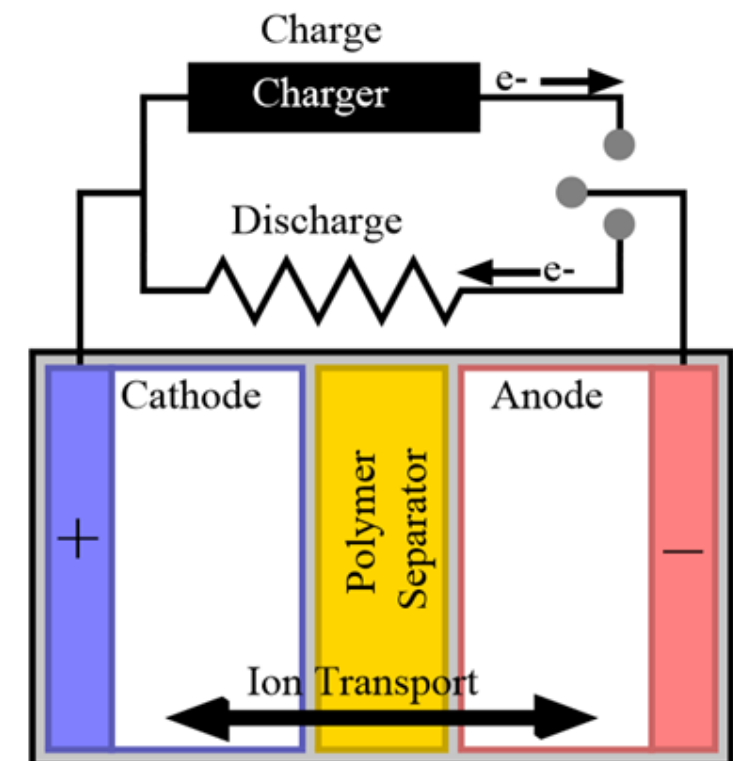
I would like to thank the DOE's **Office of Electricity** and **Dr. Imre Gyuk, Program Manager of the Electrical Energy Storage Program**, for their support and funding of the Energy Storage Program.

Project Overview

In the Energy Storage Program, we are developing electrical energy storage solutions to develop a more efficient, reliable and secure electricity network.

There has been large investments made in a variety of electrochemical storage due to its fast response times, energy-power capacity and lifetimes

Electrochemical storage: Li ion, sodium-halide, hybrid Pb acid, flow batteries (aqueous and non aqueous) and electrochemical (EC) hydrogen production



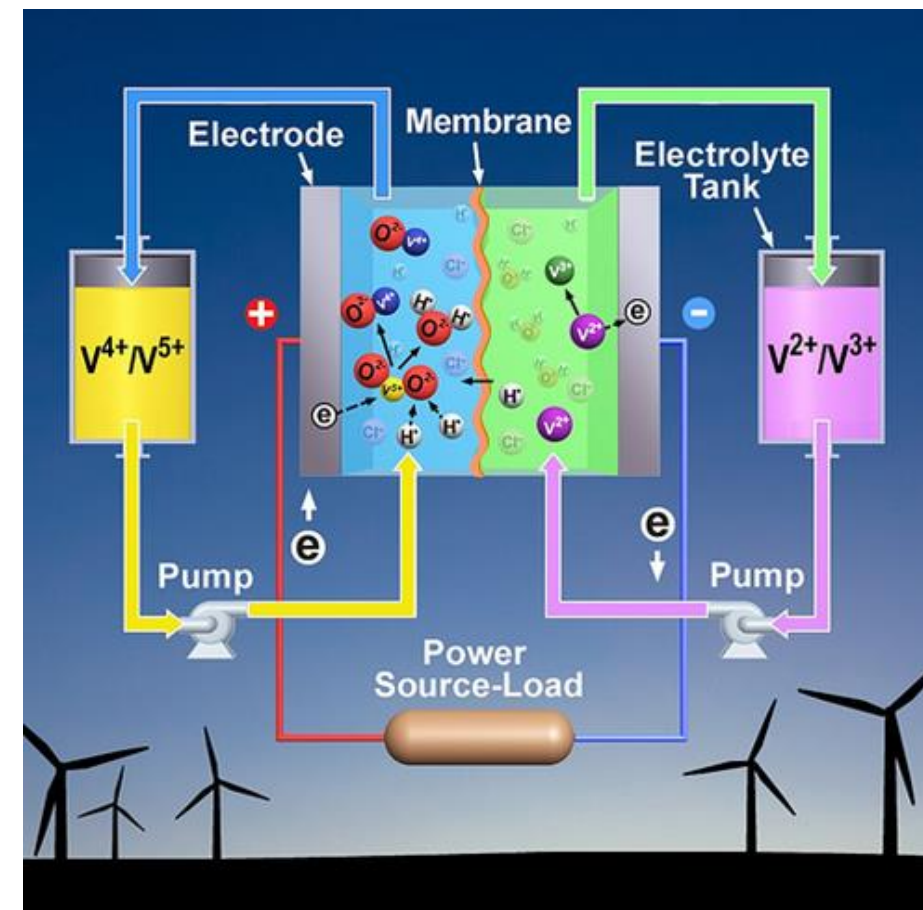
Both flow batteries and EC hydrogen production typically Nafion is used as a separator due to good performance and durability. However, cost is an issue (\$250-500/m²)!

Partnering with industry is important to show relevance. From last year meeting in SD, ARPA-e recipient ProtonOnsite had interest in materials being developed.

Funds-in via Work for Others with ProtonOnsite

Project

- Separation of energy and power
- Robust battery. Allows for deep discharge, long life cycles and little capacity fade
- VRB Proven technology – UniEnergy plans for 3.5MW of total storage
- Several companies looking to commercialize the technology



UET UniEnergy Technologies

 WattJoule

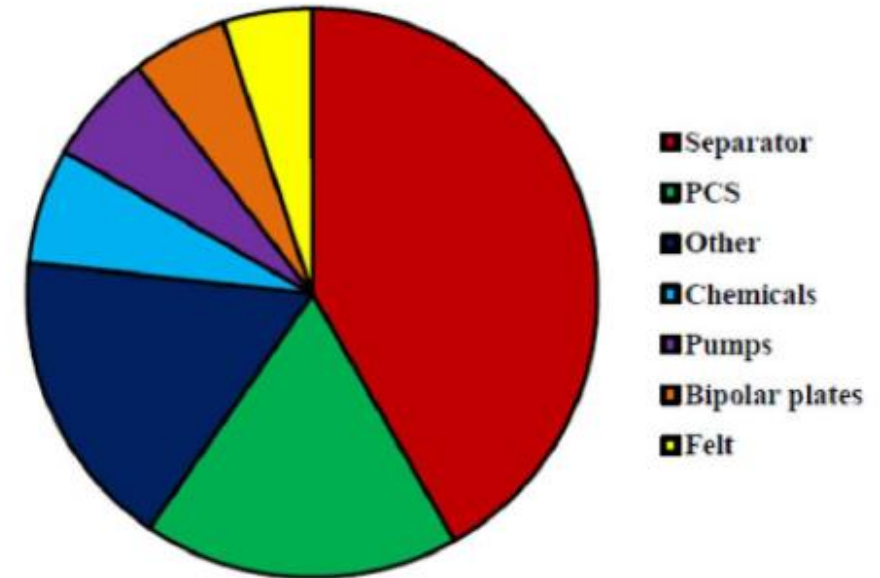
IMERGY™ POWER SYSTEMS

Cost is focus since current capital costs range between \$500-800/kWh

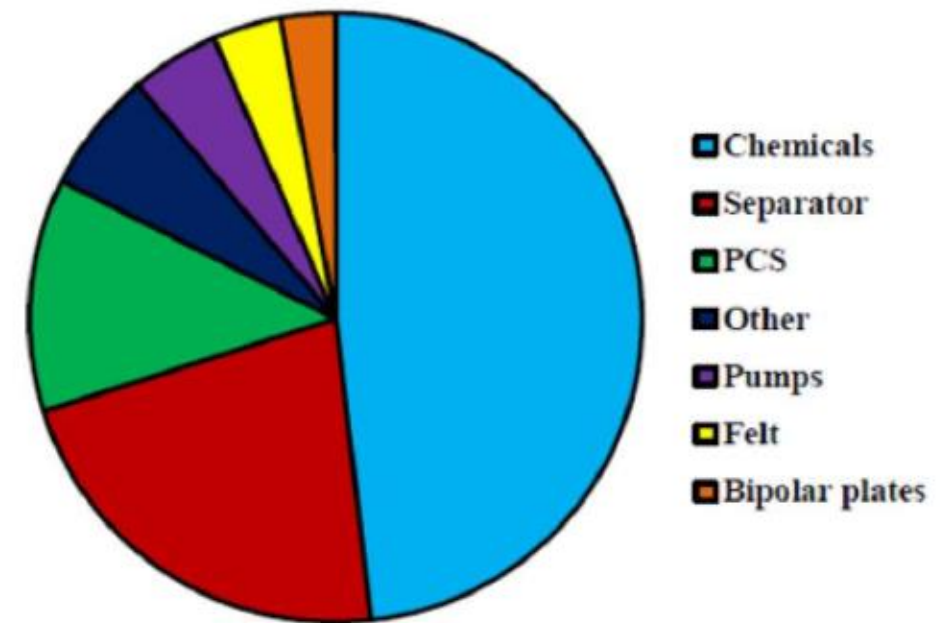
Cost of VRB

- New cost model by PNNL. Cost calculated based on shunt-pumping losses and delivered power and energy capacity.
- Two type of VRB
 1. Power intensive: 1 MW/0.25 MWh (Power quality applications)
 2. Energy intensive: 1 MW/4 MWh (Load following)
- In both scenarios the membrane separator takes up a significant portion of total cost
- Nafion™ \$250-500/m²; Perfluorinated polymer (primarily C-F)

VRB capital costs¹



Power intensive case

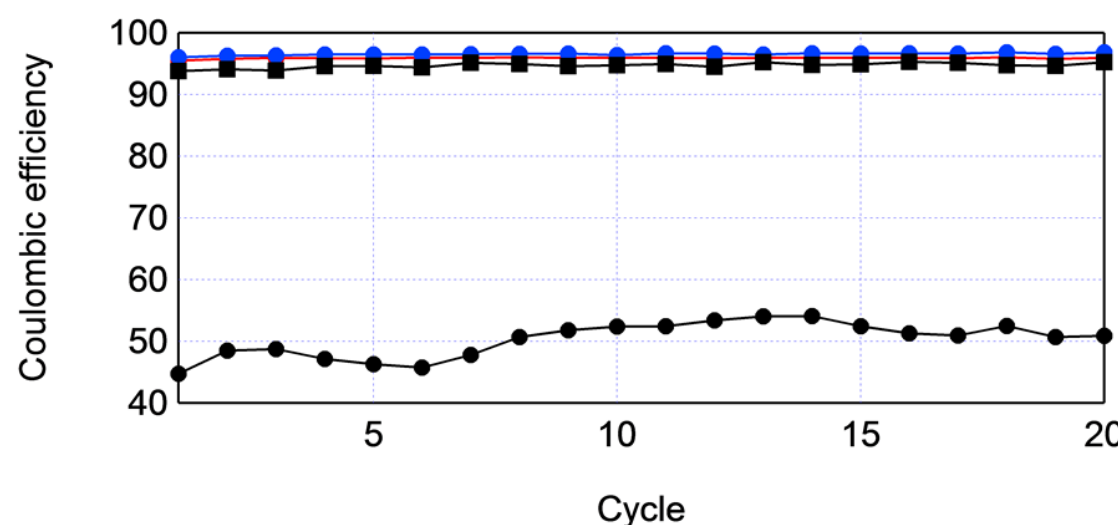
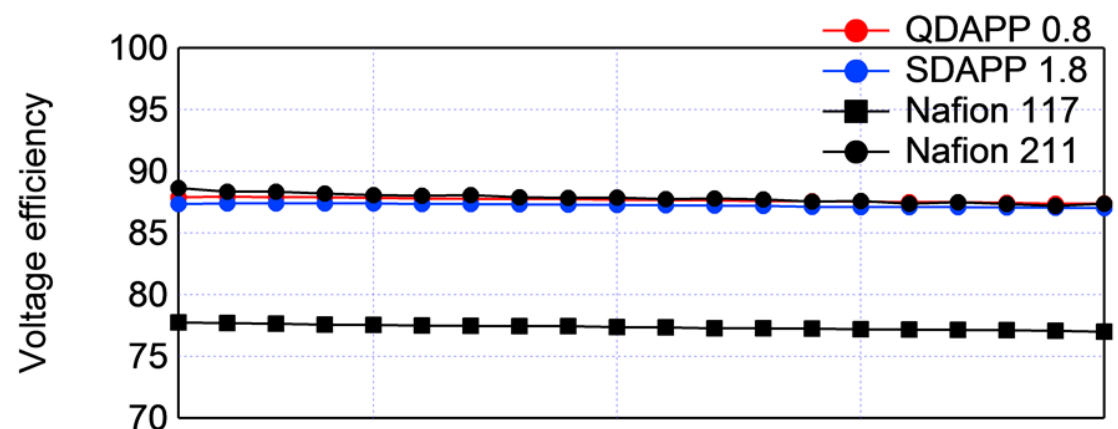
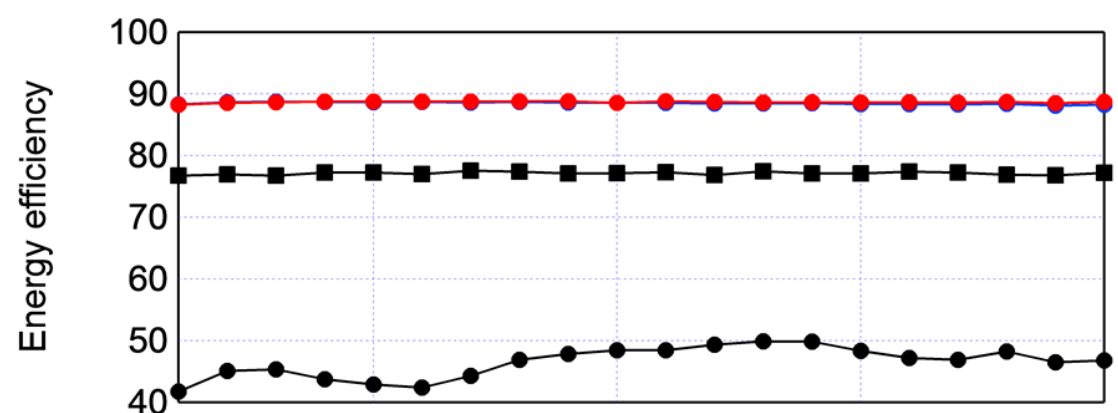
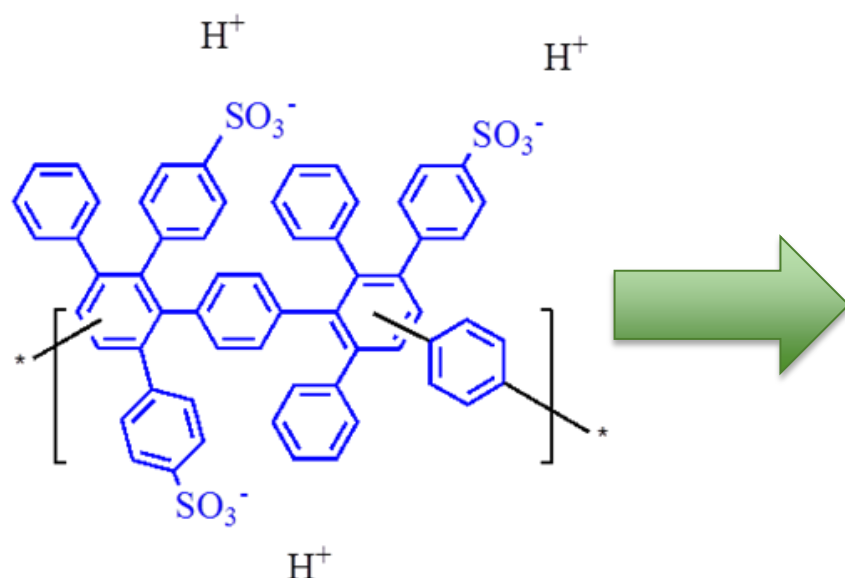


Energy intensive case

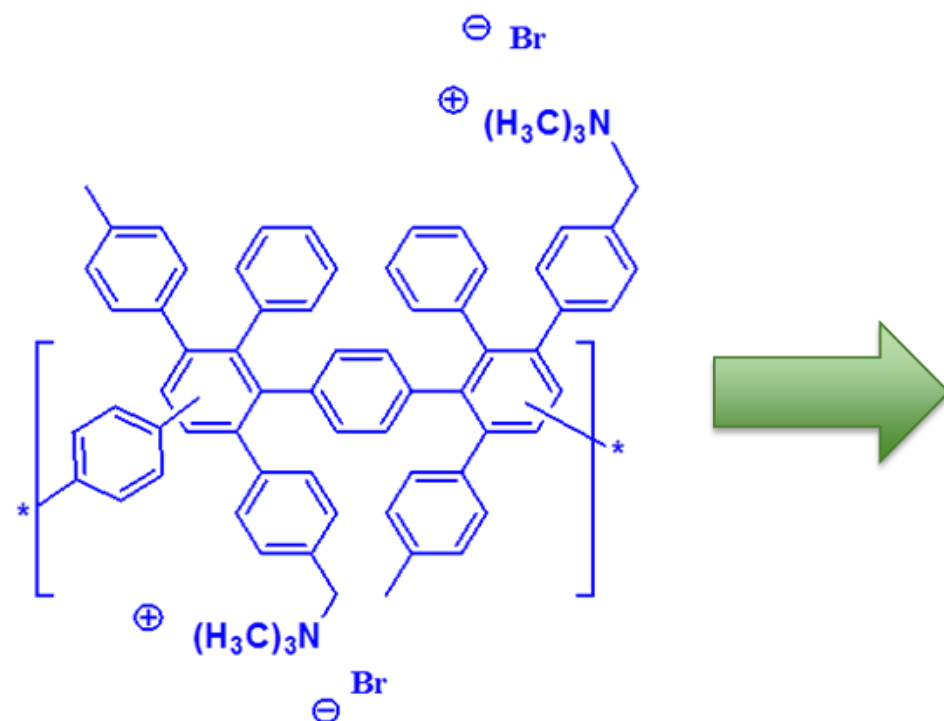
Developing hydrocarbon polymer (C-H) with equal or better performances to Nafion at a price target of \$40/m²

Membrane Performance

1st Gen: SDAPP



2nd Gen: QDAPP



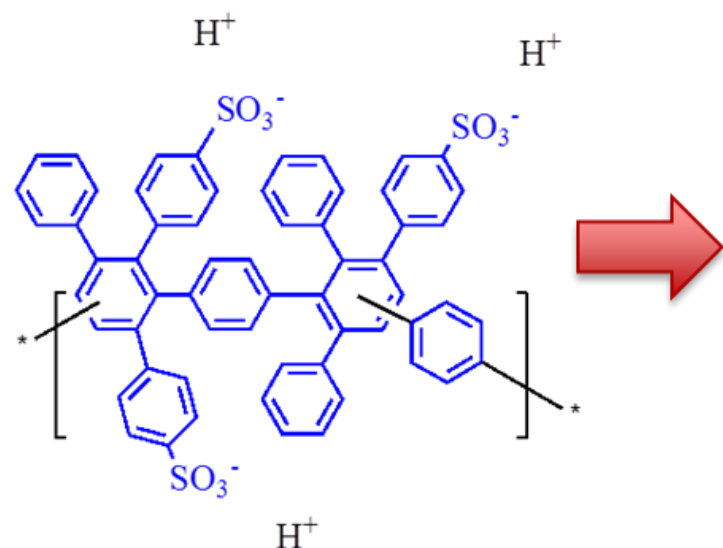
1st and 2nd Gen materials show good energy efficiency

Sun &
Pezeshiki, UT

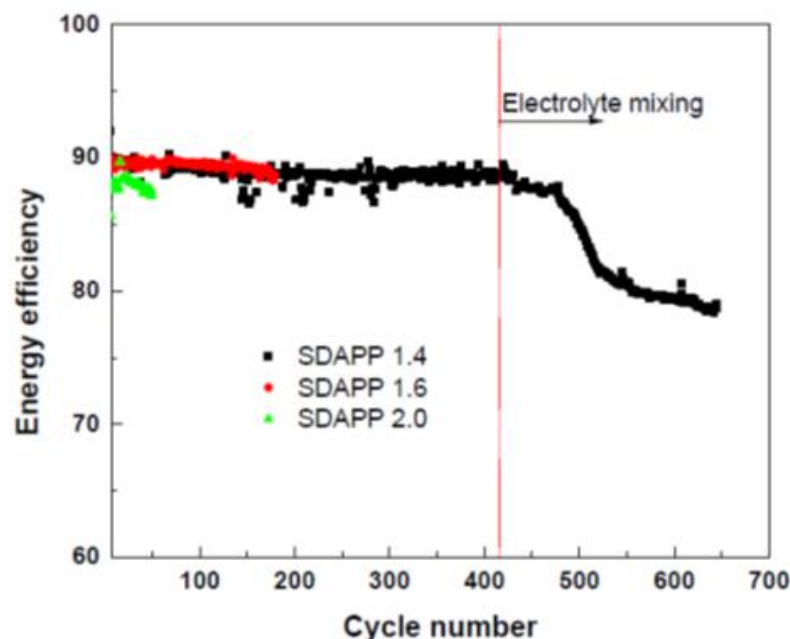
Membrane Durability

Kim, PNNL

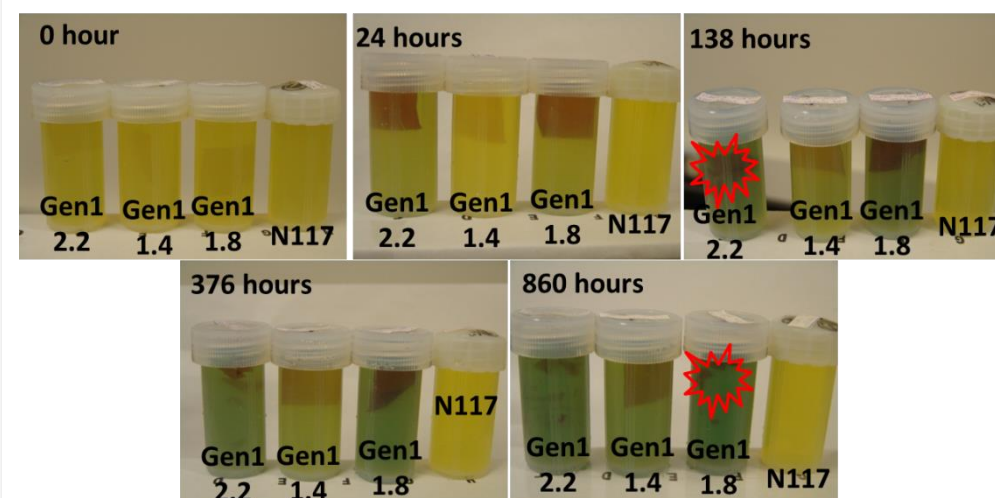
1st Gen: SDAPP



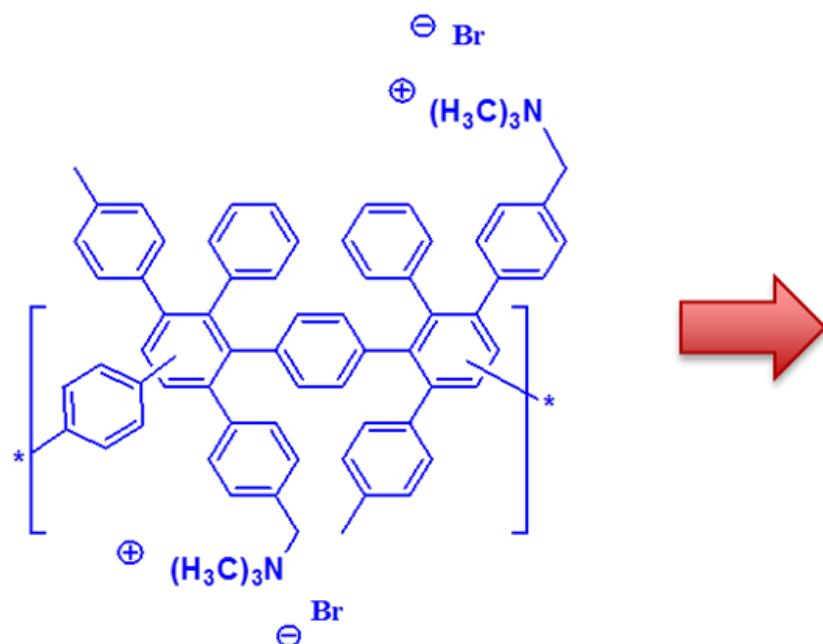
In-situ



Ex-situ: 0.1M V⁺⁵



2nd Gen: QDAPP



Ex-situ: 0.1M V⁺⁵



Sun, ORNL

Durability is primary issue with 1st and 2nd Gen materials

Fujimoto, G.; Kim, S.; Stains, R.; Wei, X.; Liyu, Li, Yang, Z. *Electrochem Comm.* 2012, 20, 48

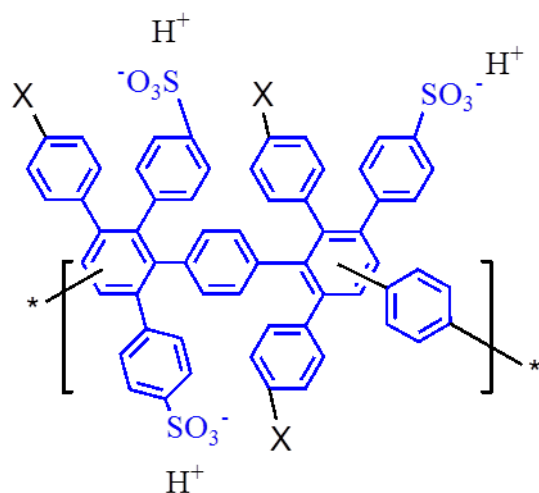
Sun, C.; Tang, Z.; Belcher, C.; Zawodzinski, T.; Fujimoto, C. *Electrochem Comm.* 2014, 43, 63

Membrane Durability

1st Gen: SDAPP

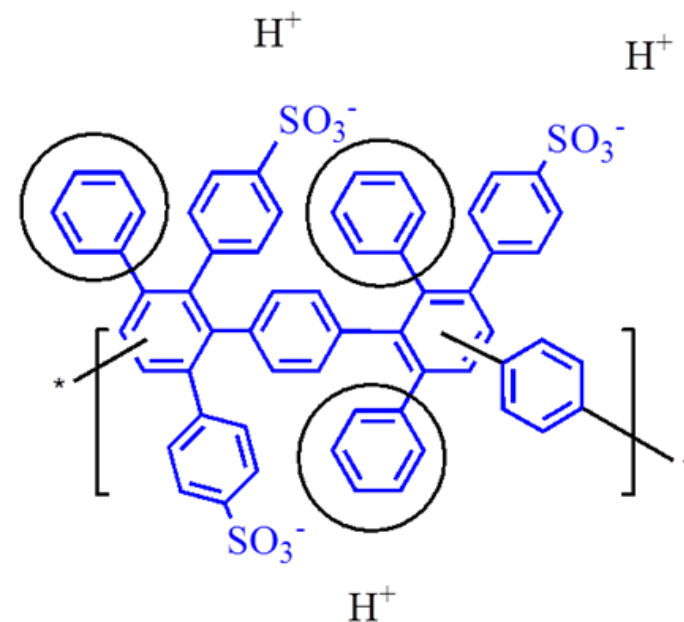
**To improve oxidation resistance,
need to reduce electron density on
the aryl rings**

Gen3: Oxidatively stable group [OSG]



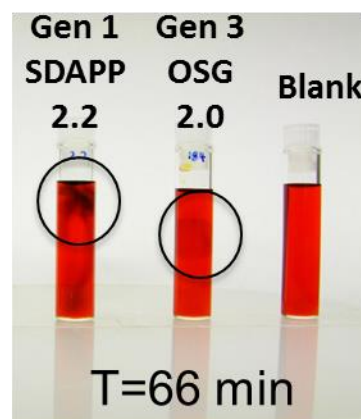
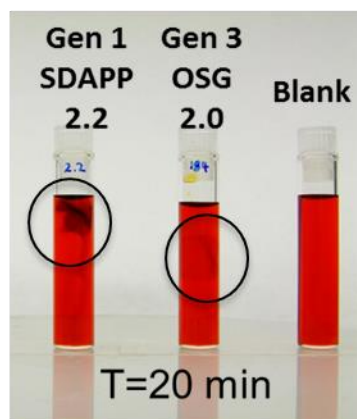
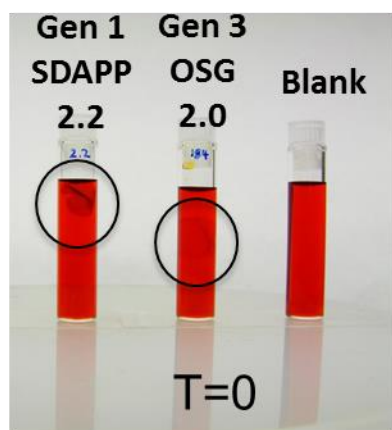
X = e⁻
withdrawing
group

Better stability than Gen 1. Submitted TA last year, preparing to file patent



Gen4 – Developed this year from lessons learned from Gen3. Submitted TA this year.

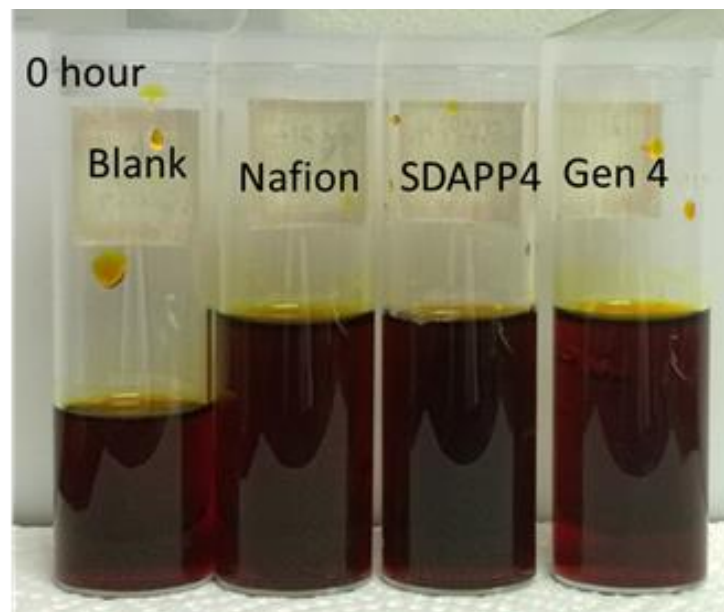
We cannot discuss structures yet, but we will cover initial testing



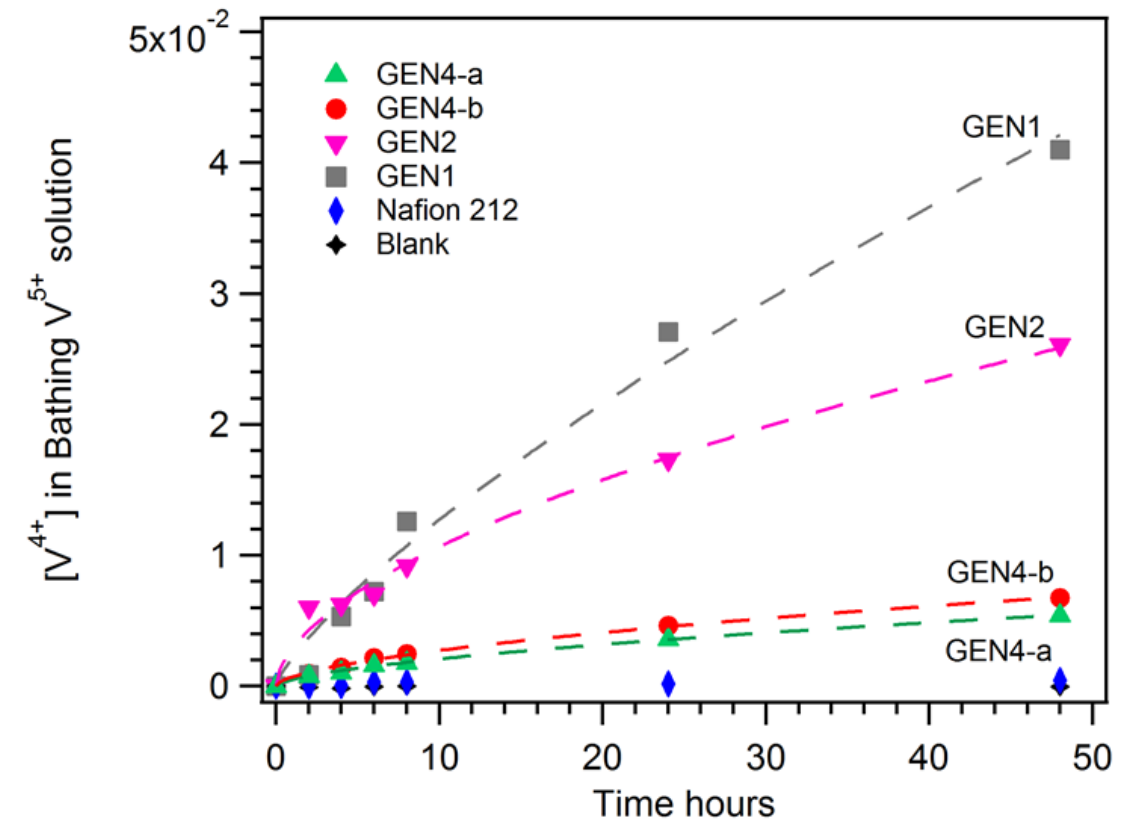
Membrane Durability

Tang, ORNL

25 mL of 1.7 M V^{+5} , 5M SO_4^{-2}
200mg of membrane



Monitored V^{+4}
production by UV-
Vis

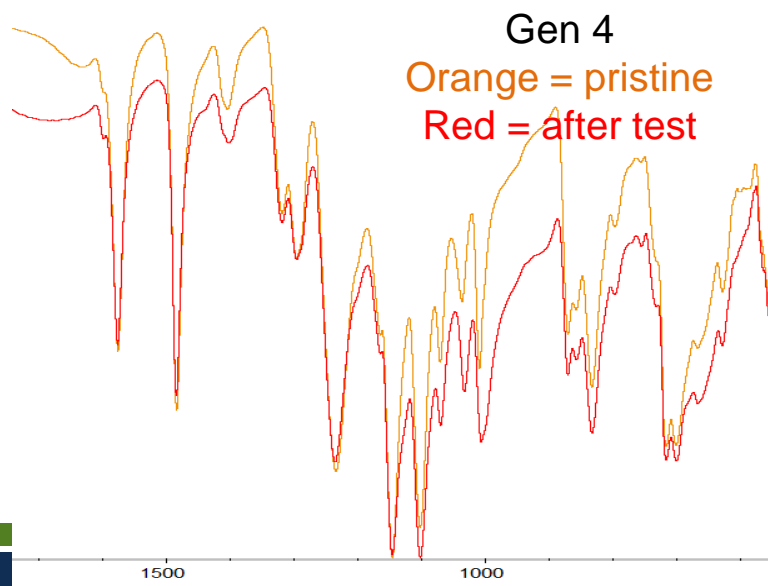
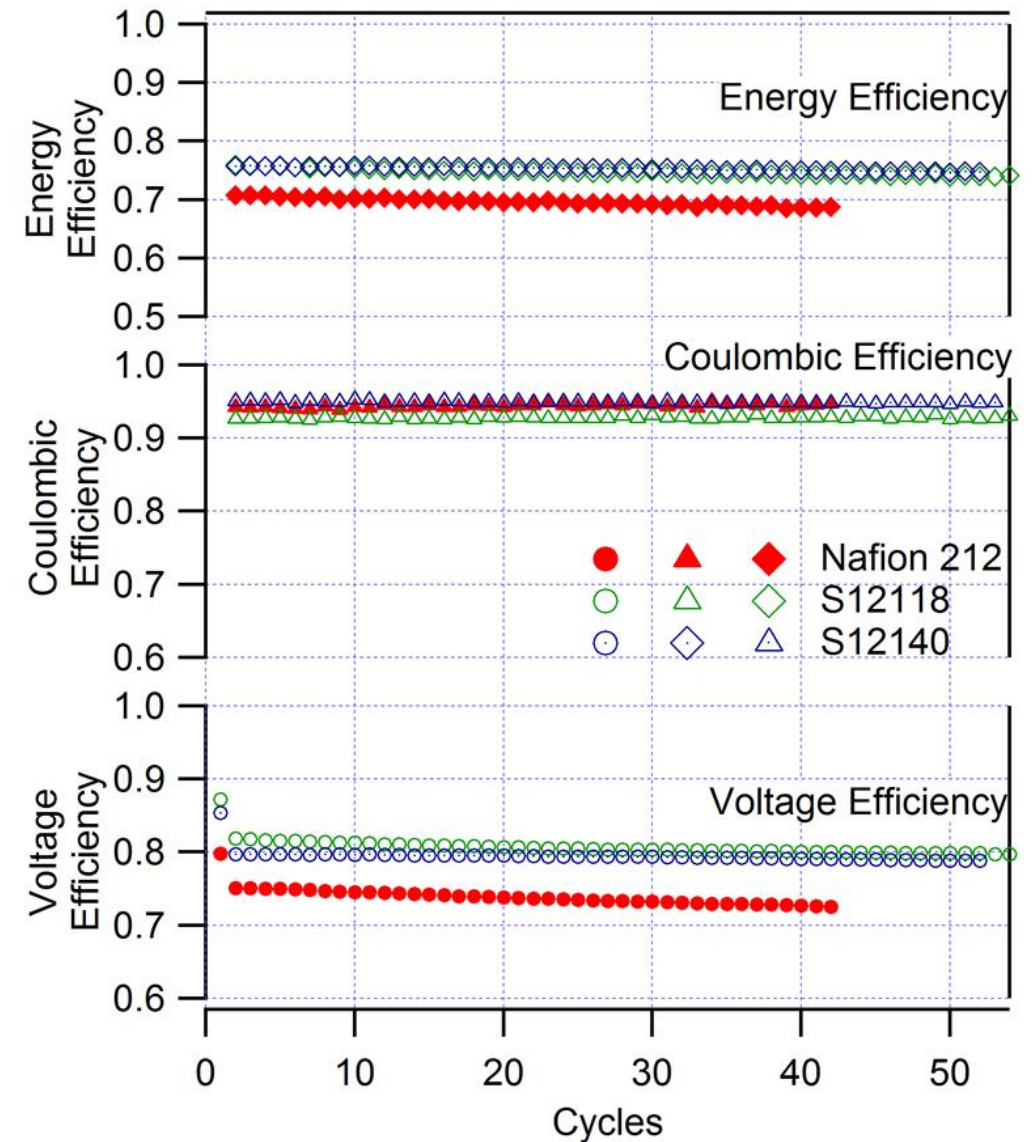
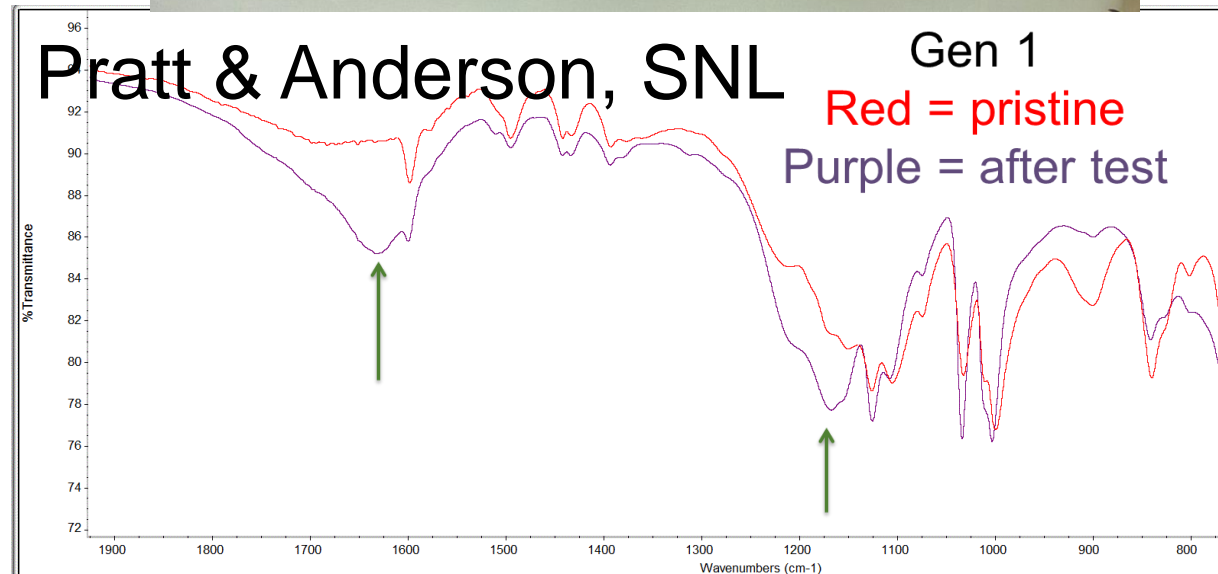
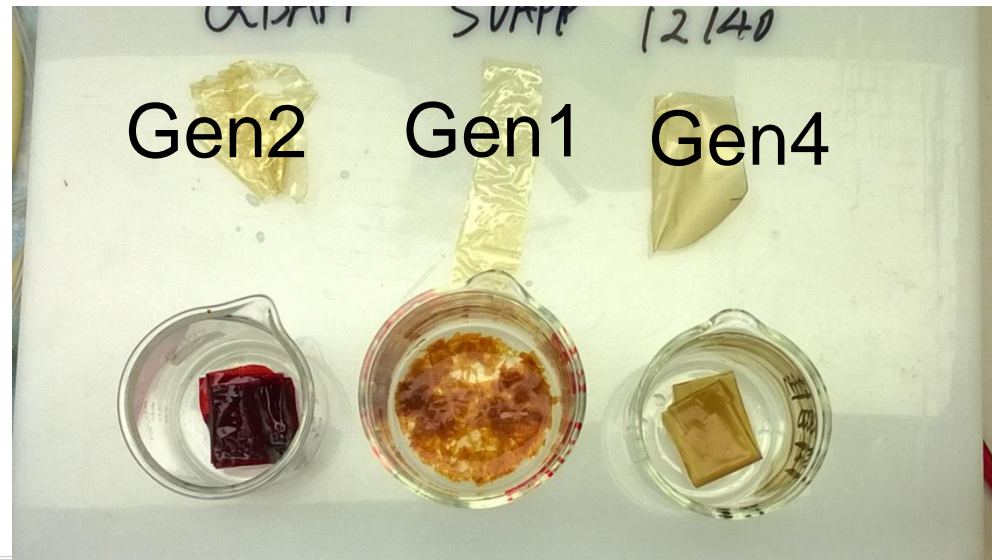


- Faster V^{+4} generation = least stable in V^{+5}
- Gen1 with fastest V^{+4} concentration increase
- Gen4 reacts over 5 times more stable than Gen1 or 2

Gen4 samples do show V^{+4} , but significantly better than Gen 1&2

Membrane Durability

Tang, ORNL



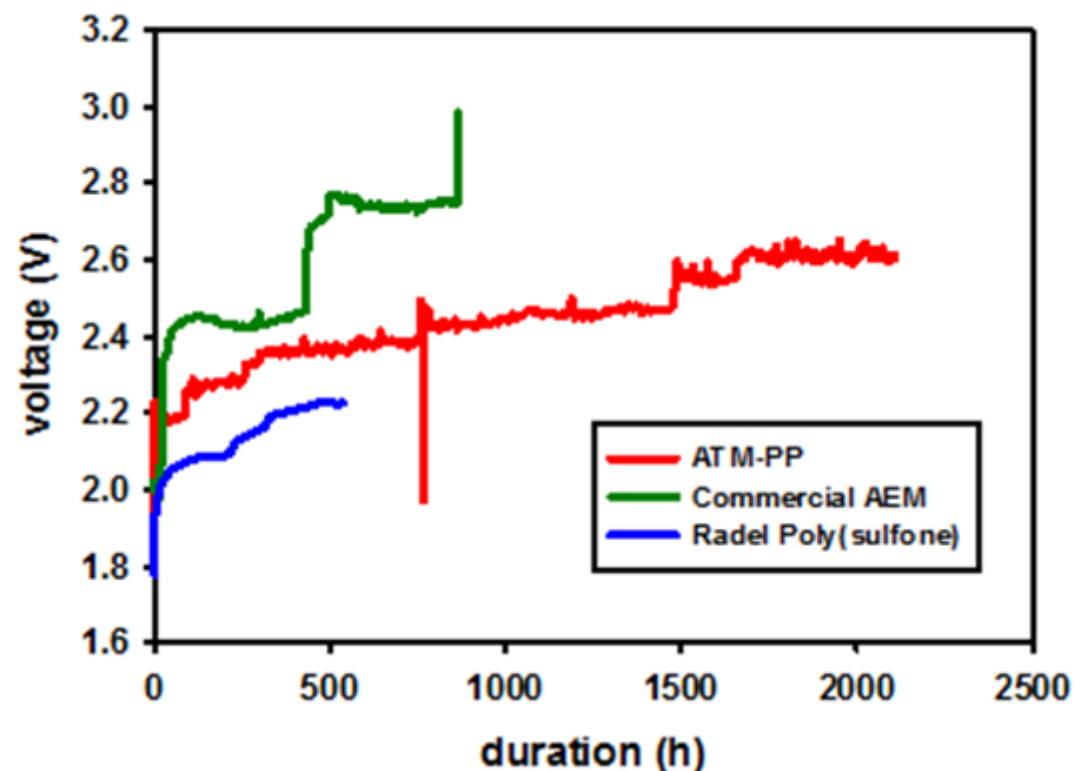
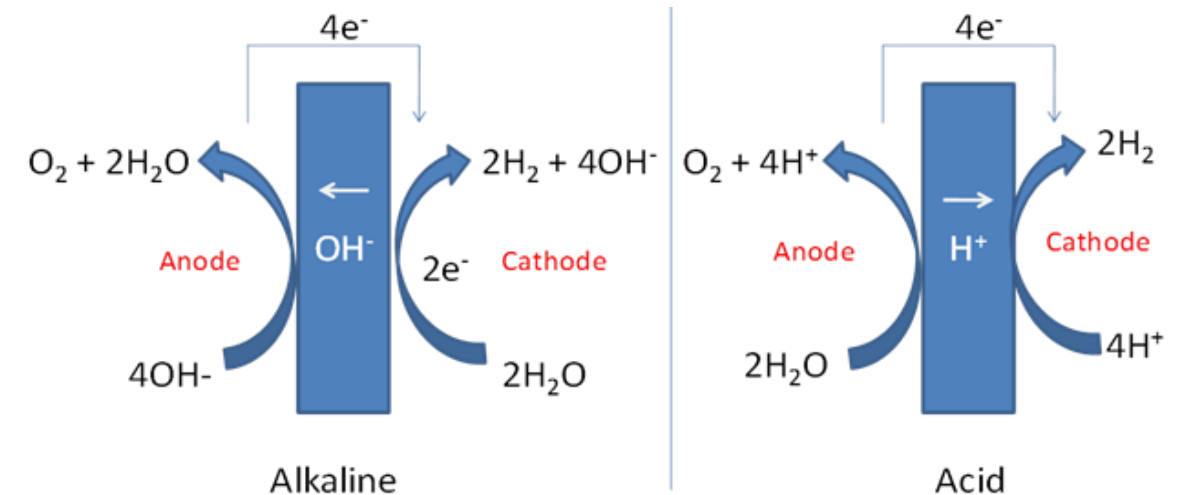
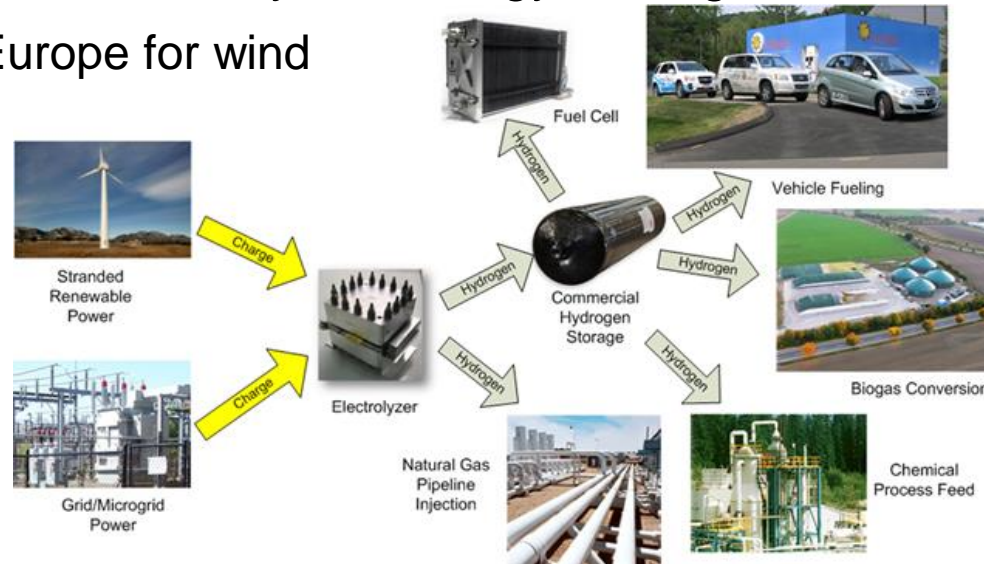
- Gen1 and Gen2 films cracked – discolored after test. Gen4 remained intact
- IR shows new peak growth in Gen1 after test. Gen4 show no changes before-after
- Gen4 slightly improved performance Nafion212

Industry Interest

Hydrogen production with zero carbon footprint through electrolysis

Leverage Hydrogen Flexibility for Energy Storage

Heavy interest in Europe for wind capture and biogas conversion



- “Traditional” water electrolysis is acidic
- Cost of Nafion and precious metal catalysts (Pt and Ir) drive cost of technology
- Alkaline, basic conditions allow use of non precious metal catalysts and lower cost
- No stable alkaline separator material available
- Desired lowest voltage for hydrogen production and no catastrophic failure
- Radel failed after 500 hrs, commercial AEM failed near 1000 hrs, Sandia (ATM-PP) over 2000 hrs (never failed, test halted)

Lifetime is very promising, some work needs to be done in lowering operational voltages

FY14 Accomplishments

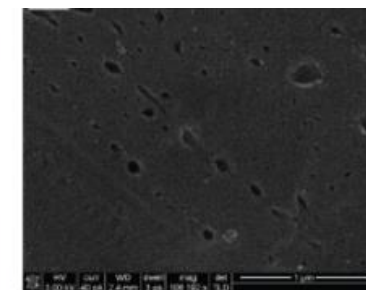
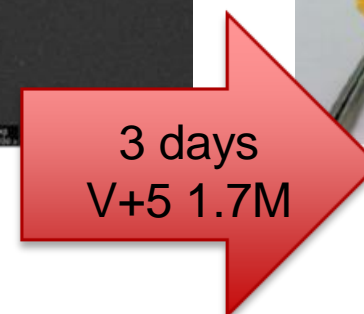
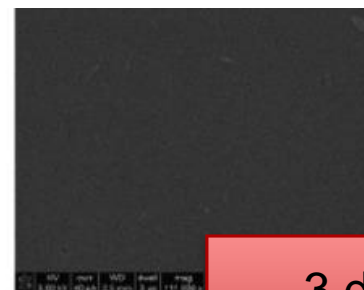
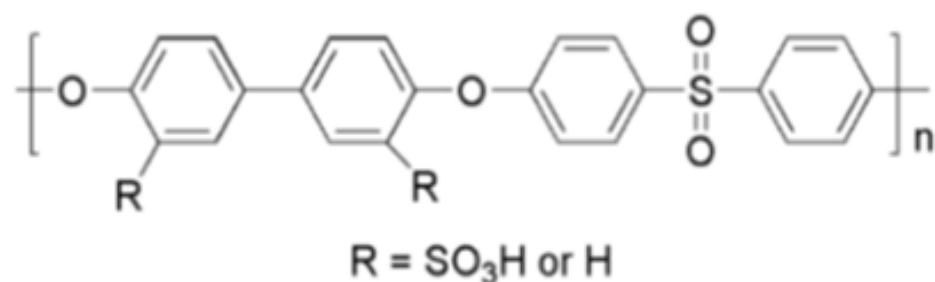
- Gen4 significantly improved durability over Gen 1&2
- Gen4 VRB performance (EE and VE) are better than Nafion212
- Patent filing on Gen3 and Gen4 soon to follow

Future Tasks

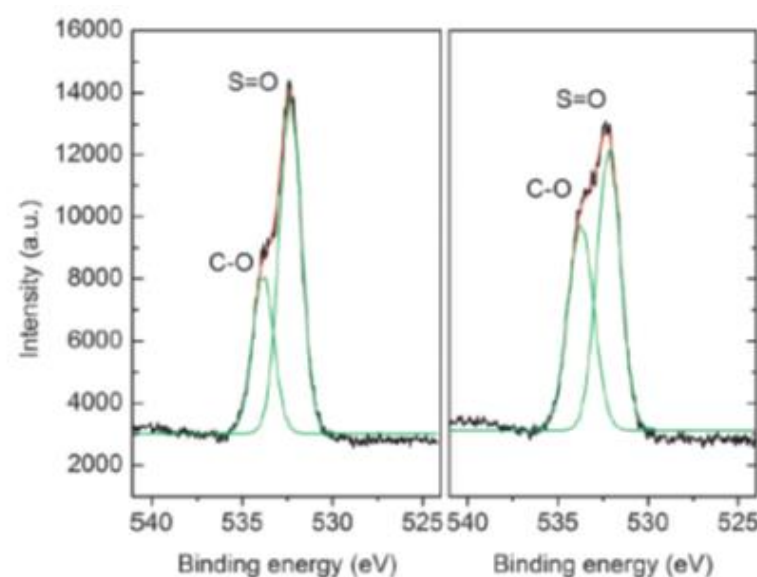
- Long term VRB testing for Gen3 and 4
- Long term ex situ (month) with UV-vis and IR analysis
- Work with industry to promote other electrochemical technologies to implement Gen3 and 4

Contact: chfujim@sandia.gov

Membrane Durability

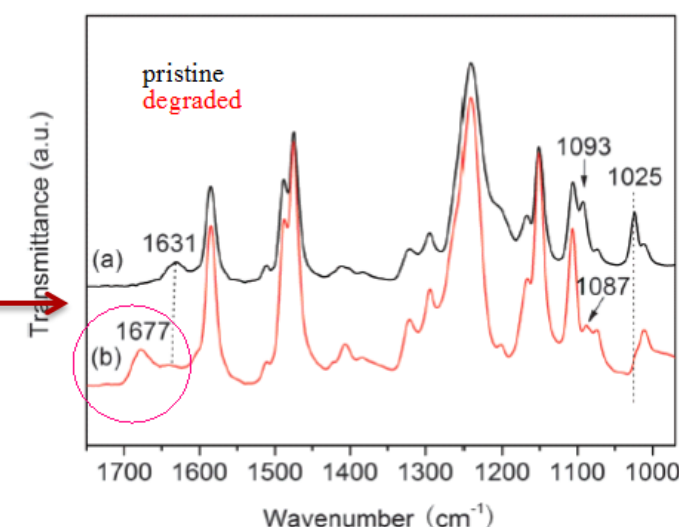


XPS O1s spectra show increase of concentration C-O content of degraded film



pristine degraded

Authors speculate that new peak in IR of degraded sample fall in the range of quinone



Although the degraded S-Radel was not fully characterized, study does prove V+5 is a strong enough to oxidize backbone – Can we design polymer backbone to resistance oxidation